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APPLICATION NUMBER: 60/540,612

FILING DATE: *January 30, 2004*

RELATED PCT APPLICATION NUMBER: PCT/US05/03433



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15536 U.S. PTO  
60/540612  
013004

Date 01 / 30 / 04

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Docket Number:

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EL 979978869

SECOND SHEET OF INVENTORS

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EL 979978869

# FEE TRANSMITTAL

for FY 2000

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See 37 C.F.R. §§ 1.27 and 1.28.

TOTAL AMOUNT OF PAYMENT (\$) 160.00

## Complete if Known

Application Number Filed Herewith  
Filing Date Filed Herewith  
First Named Inventor Stephan M. Brandstadter  
Examiner Name Unknown  
Group / Art Unit Unknown  
Attorney Docket No. PC3-046

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### 1. BASIC FILING FEE

Large Entity	Small Entity	Fee Code (\$)	Fee Code (\$)	Fee Description	Fee Paid
101	690	201	345	Utility filing fee	
106	310	206	155	Design filing fee	
107	480	207	240	Plant filing fee	
108	690	208	345	Reissue filing fee	
114	150	214	75	Provisional filing fee	160.00

SUBTOTAL (1) (\$) 160.00

### 2. EXTRA CLAIM FEES

Total Claims	Extra Claims	Fee from below	Fee Paid
independent	20** =	X	0
Claims	3** =	X	0
Multiple Dependent		X	0

\*\*or number previously paid, if greater. For Reissues, see below

Large Entity	Small Entity	Fee Code (\$)	Fee Code (\$)	Fee Description	Fee Paid
103	18	203	9	Claims in excess of 20	
102	78	202	39	Independent claims in excess of 3	
104	260	204	130	Multiple dependent claim, if not paid	
109	78	209	39	** Reissue independent claims over original patent	
110	18	210	9	** Reissue claims in excess of 20 and over original patent	

SUBTOTAL (2) (\$) 0.00

## FEE CALCULATION (continued)

### 3. ADDITIONAL FEES

Large Entity	Small Entity	Fee Code (\$)	Fee Code (\$)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	0.00
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	0.00
139	130	139	130	Non-English specification	0.00
147	2,520	147	2,520	For filing a request for reexamination	0.00
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	0.00
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	0.00
115	110	215	55	Extension for reply within first month	0.00
116	380	216	190	Extension for reply within second month	0.00
117	870	217	435	Extension for reply within third month	0.00
118	1,360	218	680	Extension for reply within fourth month	0.00
128	1,850	228	925	Extension for reply within fifth month	0.00
119	300	219	150	Notice of Appeal	0.00
120	300	220	150	Filing a brief in support of an appeal	0.00
121	260	221	130	Request for oral hearing	0.00
138	1,510	138	1,510	Petition to institute a public use proceeding	0.00
140	110	240	55	Petition to revive - unavoidable	0.00
141	1,210	241	605	Petition to revive - unintentional	0.00
142	1,210	242	605	Utility issue fee (or reissue)	0.00
143	430	243	215	Design issue fee	0.00
144	580	244	290	Plant issue fee	0.00
122	130	122	130	Petitions to the Commissioner	0.00
123	50	123	50	Petitions related to provisional applications	0.00
126	240	126	240	Submission of information Disclosure Stmt	0.00
581	40	581	40	Recording each patent assignment per property (times number of properties)	0.00
146	690	246	345	Filing a submission after final rejection (37 CFR § 1.129(a))	0.00
149*	690	249	345	For each additional invention to be examined (37 CFR § 1.129(b))	0.00
Other fee (specify) _____					0.00
Other fee (specify) _____					0.00

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## SUBMITTED BY

Name (Print/Type) Robert C. Hyslop

Signature

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46,791

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Telephone 509-624-4276

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

**PROVISIONAL PATENT APPLICATION**

\* \* \* \* \*

**FLUORINE FUNCTIONAL GROUPS, FLUORINE  
COMPOSITIONS, PROCESSES FOR  
MANUFACTURING FLUORINE COMPOSITIONS,  
AND MATERIAL TREATMENTS**

\* \* \* \* \*

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**ATTORNEY'S DOCKET NO. PC3-046**

**EL 979978869**

Fluorine Functional Groups, Fluorine Compositions, Processes for  
Manufacturing Fluorine Compositions, and Material Treatments

**[0001] TECHNICAL FIELD**

**[0002]** The present invention relates to the field of fluorine functional groups, fluorine compositions, processes for manufacturing fluorine compositions, and material treatments.

**[0003] BACKGROUND OF THE INVENTION**

**[0004]** Compositions such as surfactants, polymers, and urethanes have incorporated fluorinated functional groups. In certain instances these groups are incorporated to affect the performance of the composition when the composition is used as a treatment for materials and when the composition is used to enhance the performance of materials. For example, surfactants incorporating fluorinated functional groups can be used as fire extinguishants either alone or in formulations such as aqueous film forming foams (AFFF). Traditional fluorosurfactants such as perfluoro-octyl sulfonate (PFOS) have linear perfluorinated polar portions.

**[0005]** Polymers and or urethanes incorporating fluorinated functional groups have been used to treat materials. Exemplary fluorinated treatments include compositions such as Scotchguard®.

**[0006] SUMMARY OF THE INVENTION**

**[0007]** The present invention provides fluorine functional groups, fluorine compositions, processes for manufacturing fluorine compositions, and material treatments.

**[0008]** An embodiment of the present invention provides fluorinated compositions that include  $R_f$  groups. The  $R_f$  groups can have at least two terminal  $-CF_3$  groups. In exemplary embodiments, at least half of the fluorine content of the  $R_f$  group is provided by terminal  $-CF_3$  groups. An exemplary general structure for the  $R_f$  group includes  $(CF_3)_n(CF)_{(3-n)}(CF_2)_m$ , with  $n$  between 1 and 3 and  $m$  between 0 and 6.

**[0009]**  $R_f$  groups can be incorporated into compositions such as polymers, urethanes, acrylate polymers, acrylate monomers, glycols, phosphate esters, metal complexes, and fluorosurfactants.

**[0010]**  $R_f$  containing compositions can be used as disbursing agents, or to treat substrate materials such as textile fabric, textile yarns, leather, paper, plastic, sheeting, wood, ceramic clays, as well as articles of apparel, wallpaper, paper bags, cardboard boxes, porous earthenware, construction materials such as brick, stone, wood, concrete, ceramics, tile, glass, stucco, gypsum, drywall, particle board and chipboard, and substrates such as carpet, drapery, upholstery, automotive and awning fabrics, and rainwear.



**[0011] BRIEF DESCRIPTION OF THE DRAWINGS**

**[0012]** Embodiments of the invention are described below with reference to the following accompanying drawings.

**[0013]** Fig. 1 is a general view of some compositions to which  $R_1$  groups of the present invention may be incorporated.

**[0014]** Fig. 2 is a reaction scheme of an embodiment of the present invention.

**[0015]** Fig. 3 is a reaction scheme of an embodiment of the present invention.

**[0016]** Fig. 4 is a reaction scheme of an embodiment of the present invention.

**[0017]** Fig. 5 is a reaction scheme of an embodiment of the present invention.

**[0018]** Fig. 6 is a reaction scheme of an embodiment of the present invention.

**[0019] DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

**[0020]** This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

**[0021]** An embodiment of the present invention provides fluorinated compositions. These compositions include fluorinated functional groups. These fluorinated functional groups can be referred to as  $R_f$ . An aspect of the present invention provides  $R_f$  groups having at least two terminal  $-CF_3$  groups. In an exemplary embodiment, at least half of the fluorine content of the  $R_f$  groups is provided by terminal  $-CF_3$  groups. An exemplary general structure for the  $R_f$  group includes  $(CF_3)_n(CF)_{(3-n)}(CF_2)_m$ , with  $n$  being between 1 and 3 and  $m$  being between 0 and 6. Exemplary  $R_f$  groups can include functional groups such as halogens (e.g. iodine), mercaptan, thiocyanate, sulfonyl chloride, hydroxyl, acid, and acid halides. The  $R_f$  groups may also include multiple alkylene groups having a ratio of the alkylene groups to the  $-CF_3$  groups of one to one or in other aspects of the present invention two to one. Exemplary alkylene groups include methylene groups ( $-CH_2-$ ) and/or difluoroalkylene groups ( $-CF_2-$ ).

**[0022]** Referring to Fig. 1,  $R_f$  groups can be incorporated into compositions such as polymers, urethanes, acrylics including acrylate monomers and

polymers, glycols, phosphate esters, metal complexes, poly anhydrides, poly-enes, and/or fluorosurfactants.

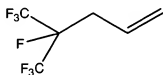
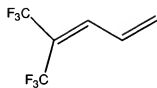
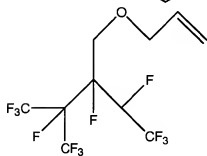
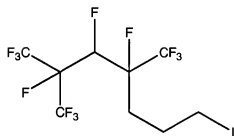
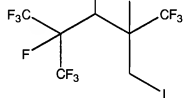
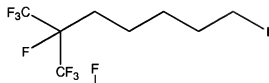
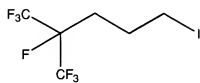
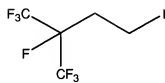
**[0023]**  $R_f$  containing compositions can be used as disbursing agents, or to treat substrate materials such as textile fabric, textile yarns, leather, paper, plastic, sheeting, wood, ceramic clays, as well as articles of apparel, wallpaper, paper bags, cardboard boxes, porous earthenware, construction materials such as brick, stone, wood, concrete, ceramics, tile, glass, stucco, gypsum, drywall, particle board and chipboard, and substrates such as carpet, drapery, upholstery, automotive and awning fabrics, and rainwear.

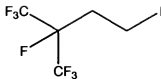
**[0024]**  $R_f$  groups can be incorporated into compositions via  $R_f$  intermediates. Exemplary  $R_f$  intermediates include a functional portion that allows for incorporation into exemplary compositions such as fluorosurfactants, metal complexes, phosphate esters, glycols, acrylics, urethanes, polymers, poly-anhydrides, and telomer-based compositions.

**[0025]** Exemplary  $R_f$  groups,  $R_f$  intermediates and compositions are described with reference to Figures 1-7. Referring to Fig. 1, a schematic view of exemplary compositions employing the  $R_f$  groups of the present invention is shown. These compositions include but are not limited to surfactants, poly-anhydrides, acrylics, urethanes, metal complexes, poly-enes, and/or phosphate esters. In exemplary implementations these compositions can demonstrate desirable surface energies. Exemplary

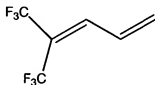
compositions having the  $R_f$  groups of the present invention can affect the surface tension of solutions in which they are incorporated and/or the water resistance of materials to which they are applied.

**[0026]** Exemplary  $R_f$  intermediates include but are not limited to the following:





[0027] The  $R_I$  intermediate (4-iodo-2-(trifluoromethyl)-1,1,1,2-tetrafluorobutane) may be obtained for example at Matrix Scientific, P.O. Box 25067, Columbia, SC 92994-5067.



[0028] The  $R_I$  intermediate (1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene) can be prepared in an exemplary aspect according to J. Org. Chem., Vol. 35, No. 6, 1970, pp. 2096-2099 herein incorporated by reference. 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene can also be prepared according to the following example.

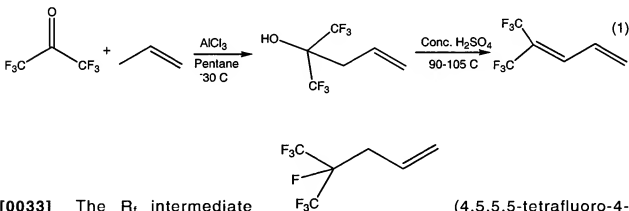
[0029] **Exemplary preparation of 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene.**

[0030] Pentane (300cc) is placed in a 500cc three neck flask. The pentane is chilled below  $-30^{\circ}\text{C}$ . To the pentane is added hexafluoroacetone (59g, 0.36mol), propylene (16.2g, 0.38mol.), and anhydrous aluminum trichloride (0.77g, 0.006mol). This solution is stirred and the temperature is allowed to warm to room temperature over 3 hour period.

[0031] A 15% aqueous HCl solution (20 mls) is added to the mixture and the mixture is washed 3 times with  $\text{H}_2\text{O}$ . The aqueous layer is decanted off

and the organic layer is dried with  $\text{MgSO}_4$ . Remaining pentane and propylene are flashed vaporized off at  $60^\circ\text{C}$  to give 54.4 grams (70% by Gas Chromatography) of isomeric 1,1-bis(trifluoromethyl)-3-penten-1-ol.

**[0032]** The crude 1,1-bis(trifluoromethyl)-3-penten-1-ol (54 grams) is placed in a 250ml 3-neck flask. To this is added 125ml of conc.  $\text{H}_2\text{SO}_4$ . The stirred solution is heated slowly to  $95^\circ\text{C}$  (the lights are boiled off between  $34$  and  $55^\circ\text{C}$ ). The product 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene (15.6g, 45.5% yield) is taken off between  $70$  and  $74^\circ\text{C}$ . A process scheme for the preparation of 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene is shown below as exemplary reaction sequence(1).



**[0033]** The  $\text{R}_f$  intermediate (4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene) can be prepared in an exemplary aspect according to Synthesis and characterization of a new class of perfluorinated alkanes: tetrakis(perfluoroalkyl) alkane. G. Gambaretto et al., Journal of Fluorine Chemistry, 5892 (2003) pgs 1-7 and United States Patent 3,843,735 to Knell et al both of which are herein incorporated by reference. 4,5,5,5-

tetrafluoro-4-(trifluoromethyl)pent-1-ene can also be prepared according to the following example.

**[0034] Exemplary preparation of**  
**4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene.**

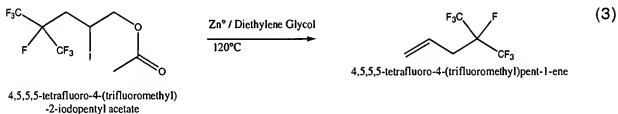
**[0035]** 1,1,1,2,3,3,3-heptafluoro-2-iodopropane (1651g, 5.6mol) AIBN (9.2g, 0.06mol), and 293g of 30% aqueous  $\text{Na}_2\text{S}_2\text{O}_5$  are placed into a 2L pressure reactor. The reactor is sealed and heated to 80°C under autogeneous pressure. Allyl acetate (587g, 5.9mol) is slowly added to this mixture and the mixture is stirred for an additional 4 hours.

**[0036]** After stirring the organic layer is removed, washed twice with  $\text{H}_2\text{O}$  and dried with  $\text{MgSO}_4$  to give 2212g of 4,5,5,5-tetrafluoro-4-(trifluoromethyl)-2-iodopentyl acetate (94%).

**[0037]** Diethylene glycol (2944g) and zinc powder (1330g) are placed into a 5L 5-neck flask equipped with a simple distillation apparatus. This mixture is stirred and heated to 120°C and the 4,5,5,5-tetrafluoro-4-(trifluoromethyl)-2-iodopentyl acetate (4149g) is slowly added. As the 4,5,5,5-tetrafluoro-4-(trifluoromethyl)-2-iodopentyl acetate is added, 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene (2075g, 97.8% assay by gc) is flashed-off and collected in a 1L ice trap. The content of the ice trap is distilled to give 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene >99.5% (b.p. 54°C). A



process scheme for the preparation of 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene is shown below as exemplary reaction sequence (2) and (3).

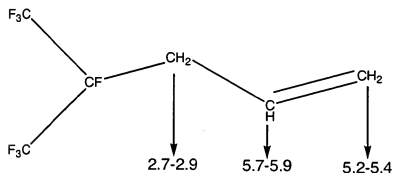


**[0038]** Gas Chromatography, Gas Chromatography/Mass Spectrometry and  $\text{H}^1$  NMR is utilized to determine 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene as shown below.

Gas Chromatography of 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene				
Compound	Dbwax® (min)	Area %	Silicaplott® (min)	Area %
F7I	2.7, 3.6	0.8, 99.2		
allylOAc	13.1	99.9		
Iodoacetate	24.5	95+	N/A	
perfluoroisopropyl-1-propene	3.1	97.8+	23.4	99+

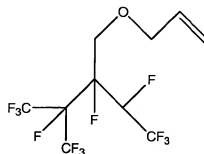
Gas Chromatography / Mass Spec of 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene		
Compound	SilicaPlot (min)	m/z
F7I	12.5 – 13.6	295-300
perfluoroisopropyl- 1-propene	14.9	210

[0039] NMR  $H^1$  Chemical Shifts (ppm) of 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene.



[0040] The  $R_I$  intermediate

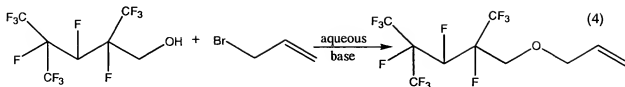
(2,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl) Pentyl allyl ether) can be



prepared in an exemplary aspect according to the following exemplary method.

**[0041] Exemplary Preparation of 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl)**

**[0042]** 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl) pentanol (551g, 1.66 moles) (exemplary procedures for the preparation of which are disclosed in US 3,467,247, herein incorporated by reference), allyl bromide (221.2g, 1.83 moles) and tetrabutylammonium hydrogen sulfate (5%) are placed into a 1L three-neck flask. This mixture is chilled to 10°C and 50% KOH (400g) is added over a 2 hour period. This solution is allowed to stir at 10°C for 72 hours. After the 72 hours an additional 100ml of 33% KOH is added and the mixture is allowed to stir for an additional 12 hours. The reaction is monitored by gas chromatography and after the reaction of 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl) pentanol the mixture is washed 1 x H<sub>2</sub>O, 2 x 10% HCl and 1 x H<sub>2</sub>O. The organic layer is dried with MgSO<sub>4</sub> to give 516 g of material containing 20.04 and 28.21% (by gas chromatography and gas chromatography/mass spectrometry) 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl) pentyl allyl ether. A process scheme for the preparation of 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl) pentyl allyl ether is shown below as exemplary reaction sequence (4).



**[0043]** Iodide  $R_I$  intermediates can be converted to thiocyanate  $R_I$  intermediates ( $R_I\text{SCN}$ ) by reacting the iodide intermediate with potassium thiocyanate as shown below as exemplary reaction sequence (5) and described as follows:



**[0045]** The reaction is carried out in absolute ethanol using acetic acid as a catalyst. A 30% molar excess of KSCN as compared to  $R_I\text{I}$  is used. The ethanol, acetic acid,  $R_I\text{I}$ , and KSCN are charged to a reaction vessel, heated to reflux and held there until the reaction is complete. The reaction progress is monitored by analyzing the reaction mixture for  $R_I\text{I}$  by gas chromatography. Upon reaction completion, the KI is filtered off the reaction mixture, the ethanol is evaporated away and the  $R_I\text{I}$  is washed twice with hot (70 °C) water.

**[0046]** A mercaptan  $R_I$  intermediate may also be produced by reacting the iodine  $R_I$  intermediate with thiourea to make the isothiuronium salt and treating the isothiuronium salt with sodium hydroxide to give the mercaptan

$R_f$  intermediate plus sodium iodide, as described in U.S. patent 3,544,663 herein incorporated by reference.

**[0047]** An embodiment of the present invention provides fluorosurfactants that include the  $R_f$  groups described above. Exemplary surfactants include those compounds having a polar portion attached to a non-polar portion. The polar portion can be referred to as the tail of the surfactant and the non-polar portion can be referred to as the head of the surfactant. Fluorosurfactants ( $R_f$ - $R_s$ ) include those surfactants having tail or polar portions containing fluorine. The fluorosurfactant tail or polar portion can be referred to as an  $R_f$  portion and the fluorosurfactant head or non-polar portion can be referred to as an  $R_s$  portion.

**[0048]** Aspects of the present invention provide fluorosurfactant production methods as well as fluorosurfactant intermediates and methods of manufacturing fluorosurfactant intermediates. An exemplary fluorosurfactant production method includes providing a fluorosurfactant intermediate having at least two  $-CF_3$  groups. Exemplary fluorosurfactant intermediates include fluorocarbons having a beta end and an alpha end with the alpha end being designated for later attachment to the  $R_s$  portion of the fluorosurfactant. Exemplary methods for preparing surfactants can be found in German Offen. 1,924,264 and U.S. Patent 3,721,706 both of which are hereby incorporated by reference. Exemplary methods for preparing fluorosurfactants that include the  $R_f$  groups of the present invention are described below.

**[0049]** The thiocyanate  $R_1$  intermediate can be wet chlorinated to give the sulfonylchloride of the fluorosurfactant intermediate as shown below in exemplary reaction sequence (6).



**[0050]** The  $R_1SCN$ , water and acetic acid as a solvent are charged to a reaction vessel. Chlorine is added to the reaction vessel in 30 minute increments while the reaction vessel temperature is maintained at 20 °C to 30 °C. At the end of each 30 minutes of chlorine addition, 0.314 grams of water is added to the reaction vessel. For each gram of chlorine that is added, 4.5 moles per mole of  $R_1SCN$  is added. When this amount has been added, the reaction mixture is sampled and analyzed for  $R_1SCN$  by gas chromatography. When the reaction is complete, the reaction mixture is diluted to 65%  $R_1SO_2Cl$  with chloroform, heated to 40 °C and washed with twice its volume of 40 °C water. After the wash, the mixture is dried by azeotroping the water out using a Dean Stark trap. Karl Fischer titration is used to determine water amount. Water content can be less than 0.1%. The sulfonylchloride intermediate can then be esterified with a dimethylaminopropylamine ( $H_2N(CH_2)_3N(CH_3)_2$ , DMAPA) to yield a sulfonamidoamine as shown as exemplary reaction sequence (7) and described below.



[0051] The reaction is carried out in chloroform solution at reflux. It is preferred that the solvent and reactants in this step be as dry as possible, at least less than 0.1% by weight water. The DMAPA is dissolved in 1.5 times its volume in chloroform in the reaction flask which is immersed in a cooling bath. A DMAPA molar equivalent of 65%  $R_fSO_2Cl$  in chloroform solution is added to the reaction flask while maintaining the temperature of the reaction flask at less than 50 °C. When the addition is complete the temperature is raised to reflux and held at reflux for 5 hours. The reaction flask is then cooled to 60 °C and washed 3 times with equal volumes of 60 °C water. The chloroform is stripped under vacuum and the neat product is washed twice with 90 °C water. The reaction mix is sampled and analyzed for free DMAPA using a wet chemistry method that is specific for primary amines. The sulfonamidoamine can then be betainized with an acetate such as sodium monochloroacetate to yield the amphoteric fluorosurfactant  $R_fSO_2NH(CH_2)_3N^+(CH_3)_2$  as shown as exemplary reaction sequence (8) and described below.



[0052] The sulfonamide is dissolved in enough absolute ethanol to give a 40% solution. An equimolar amount of sodium monochloroacetate is added. The mixture is refluxed for 8 hours. It is sampled and titrated for  $OH^-$ . If  $OH^-$  is greater than  $1.5 \times 10^{-3}$  eq., the solution is refluxed for an additional hour and reanalyzed. This sequence is repeated until  $OH^-$  is less than

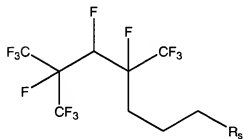
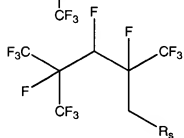
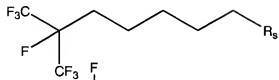
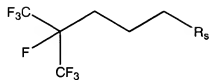
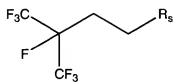
$1.5 \times 10^{-3}$  eq. If there is no decline in  $\text{OH}^-$  in two succeeding samplings, additional sodium monochloracetate is added, the amount being calculated as the amount needed to lower the  $\text{OH}^-$  to a value below  $1.5 \times 10^{-3}$  eq. The by-product NaCl is filtered off and water is then added according to the following calculation.

**[0053]** In an exemplary aspect of the present invention, the mercaptan  $\text{R}_t$  intermediate may be attached to an  $\text{R}_s$  portion such as group 2-acrylamido-2-methyl-1 propane sulfonic acid available from Lubrizol as AMPS 2403 as generally described in U.S. patent 4,000,188 herein incorporated by reference.

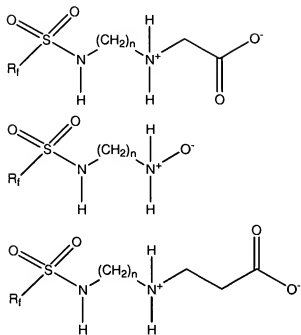
**[0054]** An exemplary method for manufacturing an aminoxide of the fluorosurfactant can include the processes as generally described in U.S. patent 4,983,769 herein incorporated by reference. Accordingly, the sulfoamidoamine is combined with ethanol and water and 70% hydrogen peroxide and heated to at least  $35^\circ\text{C}$  for 24 hours. Activated carbon is then added and the mixture refluxed for about 2 hours. The reaction mixture is filtered and the filtrate evaporated to dryness to provide the aminoxide of the fluorosurfactant.

**[0055]** Exemplary fluorosurfactants that may be produced in accordance with the methods described herein include the following:

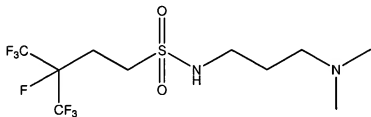




[0056] Exemplary  $R_s$  portions of the fluorosurfactants include the following:



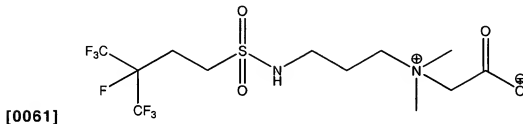
**[0057]** Exemplary fluorosurfactants include but are not limited to the following.



**[0058]** NMR:  $^1\text{H}$  (D6-DMSO, 300 MHz)  $\delta$  1.6 (m, 2H), 2.1 (bs, 6H), 2.2 (m, 2H), 2.6 (m, 2H), 2.8 (m, 2H), 3.2 (m, 2H), 7.4 (bs, 1H);  $^{13}\text{C}$  (D6-DMSO, 75 MHz)  $\delta$  22.9, 23.2, 27.5, 43.0, 45.0, 89-93 (ds), 114-126 (qd); and  $^{19}\text{F}$  ( $\text{CFCl}_3$ , D6-DMSO, 282 MHz)  $\delta$  -76.6 (bs, 6F), -183.6 (m, 1F)

**[0059]** IR: (KBr, cm<sup>-1</sup>) 3200 br w, 3100 m, 2900 m, 2800 m, 1469 s, 1315 s, 1221 s, 1160 s, 1142 m, 1083 m, 1045 m, 977, 818, 765, 713, 559 m.

**[0060]** and



**[0062]** NMR: <sup>1</sup>H (D6-DMSO, 300 MHz) δ 1.8 (m, 2H), 2.6 (m, 2H), 3.0 (m, 2H), 3.1 (bs, 6H), 3.6 (m, 2H), 3.9 (m, 4H), 7.9 (bs, 1H); <sup>13</sup>C (D6-DMSO, 75 MHz) δ 22.6, 22.9, 23.1, 43.1, 50.0, 60.8, 64.4, 88-93 (ds), 114.5-126.5 (qd); and <sup>19</sup>F (CFCl<sub>3</sub>, D6-DMSO, 282 MHz) δ -76.4 (d, 6.95 Hz, 6F), -183.4 (m, 1F)

**[0063]** The fluorosurfactants of the present invention may be used as relatively pure solutions or as mixtures with other components. An exemplary fluorosurfactant use includes use in fire-fighting foams such as aqueous film forming foams (AFFF).

**[0064]** An embodiment of the present invention provides metal complexes incorporating the R<sub>f</sub> groups of the present invention. The R<sub>f</sub> groups of the present invention can be incorporated as acid halides or carboxylic acids

(together being referred to as  $R_f$  acid) with the acid halide including, but not limited to, acid fluorides. An exemplary method for preparing the acid  $R_f$  intermediate includes reacting the iodine  $R_f$  intermediate disclosed above with fuming sulfuric acid to produce an acid fluoride  $R_f$  intermediate. Referring to Fig. 2, a reaction sequence 10 for the conversion of acid fluoride  $R_f$  intermediate 12 into a metal (chrome) complex 20 is shown. An acid fluoride  $R_f$  intermediate 12 can be reacted with an amino acid such as glycine 14 to produce an amine ester 16. Amine ester 16 may then be reacted with chromic chloride 18 in an alcohol such as methanol or isopropanol to produce an exemplary  $R_f$  chrome complex 20. Exemplary acid  $R_f$  intermediates include ethylene carboxylic acid  $R_f$  intermediates and/or mixtures of ethylene carboxylic acid  $R_f$  intermediates and carboxylic acid  $R_f$  intermediates. Exemplary preparations can be performed in accordance with U.S. Patents 3,351,643, 3,574,518, 3,907,576, 6,525,127, and 6,294,107, herein incorporated by reference.  $R_f$  chrome complexes 20 can then be used to treat substrates such as paper, leather, textiles, yarns, fabrics, glass, ceramic products, and/or metals. In some cases treating substrates with the complexes of the present invention render the substrates less permeable to water and/or oil.

[0065] An embodiment of the present invention also provides for incorporation of the  $R_f$  groups into phosphate esters which, in exemplary embodiments, can be used to treat substrates and/or be used as a disbursing agents during the preparation of polymers. Referring to Fig. 3, a

reaction sequence 30 is shown for the preparation of phosphate esters 34 from a hydroxyl  $R_I$  intermediate 32. Hydroxyl  $R_I$  intermediate 32 can be obtained by reacting iodine  $R_I$  intermediates with a strong base such as KOH. Hydroxyl  $R_I$  intermediate 32 can be reacted with  $P_2O_5$  or  $POCl_3$  in the presence of a metal (M) to yield an exemplary phosphate ester or pyrophosphate 34. U.S. Patents 2,559,749 and 2,597,702, herein incorporated by reference, generally describes the conversion of hydroxyl compounds to phosphate esters using  $P_2O_5$  or  $POCl_3$  to give partial esters. These reactions can also be carried out in the presence of pyridine as an HCl acceptor. Monoalkyl phosphates can also be prepared by treating phosphorus pentoxide  $P_2O_5$  with excess moles of hydroxyl  $R_I$  intermediate 32 followed by hydrolysis of the resulting pyrophosphate. The product can then be isolated as such or precipitated as the ammonium salt by the addition of ammonia to the reaction mixtures. Alternatively, a solution of salts of the mixed mono- and di-esters can be prepared by neutralizing a mixture of the acids with aqueous ammonia and amine or alkaline metal hydroxide.

**[0066]** Dialkyl phosphates can be prepared as well by a reaction of excess moles of hydroxyl  $R_I$  intermediate with phosphorus pentoxide (not shown). Instead of hydrolysis, however the intermediate pyrophosphate can be heated at low pressure. Alternatively,  $R_I$  phosphate esters can be prepared and separated by treating hydroxyl  $R_I$  intermediate with phosphorus pentoxide, neutralizing the resulting mixed acid phosphate with aqueous

ammonia and amine such as tetraalkyl ammonium base or alkali metal hydroxide to give a solution that can include amine or metal salts of the esters (not shown). Salts of esters can be dissolved in toluene and purged with ammonia to precipitate a mixture of the salts of the corresponding esters. The toluene and unreacted hydroxyl  $R_f$  intermediate and by-products such as the corresponding trialkyl phosphate can be removed by filtration, producing compositions having the general formula  $R_fAOPOR_p$ , as described in U.S. Patent 4,145,382 herein incorporated by reference. As used in this general formula, the  $R_f$  is the  $R_f$  group of the present invention, A is a methylene group or other similar spacer group from the phosphate ester and can be present in amounts as high as 3 and as little as none, and  $R_p$  is a corresponding salt to the phosphate including hydrogen alkali metal ammonium or substituted ammonium such as ethanol amine.

[0067] These phosphate compositions can be used as disbursing agents in the preparation of polymers or they can be diluted and used to treat substrate materials in aqueous bathes, for example, by ordinary means such as padding, dipping, impregnating, spraying, etc. These compositions can be incorporated into or used to treat such materials as textile fabric, textile yarns, leather, paper, plastic, sheeting, wood, ceramic clays, as well as manufactured articles prepared therefrom such as articles of apparel, wallpaper, paper bags, cardboard boxes, porous earthenware, etc. U.S. Patent 3,112,241 describes methods for treating materials using these phosphate esters and is herein incorporated by reference.

**[0068]** Referring again to Fig. 3, phosphate esters may also be prepared. According to reaction sequence 40 utilizing  $R_f$  epoxide intermediate 42 and/or  $R_f$  diol intermediate 44 as generally described in U.S. Patent 3,919,361 and herein incorporated by reference. Intermediates 42 and 44 can be reacted with phosphoric acid to obtain an  $R_f$  phosphoric acid ester 46. Phosphoric acid 46 can be dissolved in a solution and applied to a substrate such as paper to increase resistance to environmental materials such as oil and water. Ester 46 can also exist as a salt such as alkyl amines including ethanol amines as described in U.S. Patent 4,145,382 herein incorporated by reference. Ester 46 can be used to treat substrates such as wood pulp products including paper products such as packaging products including food packaging products.

**[0069]** An embodiment of the present invention includes the  $R_f$  group of the present invention incorporated into glycols which can be subsequently incorporated into polymers such as urethanes including polyurethane elastomers, films and coatings. Glycols having the  $R_f$  groups of the present invention can be converted to phosphoric acids or phosphate esters of those glycols as well. Referring to Fig. 4, a reaction sequence 50 for the incorporation of the  $R_f$  groups of the present invention into glycols is shown. Methods for producing these compositions are described in U.S. Patent 4,898,981, U.S. Patent 4,491,261, U.S. Patent 5,091,550 and U.S. Patent 5,132,445, all of which are herein incorporated by reference. For example and by way of example only, a mercaptan  $R_f$  intermediate 52 can be reacted

with a sulfide diol 54 or 2,6 diox-aspiro (3.3) heptane 56 to produce diols 58 and 60, respectively. Diols 58 and 60 can then be used directly or indirectly to make a condensation product 62 such as polyesters, polyureas, polycarbonates, and polyurethanes. This glycol functionality can also be incorporated into block polymers using the glycols having the  $R_f$  group of the present invention. U.S. Patent 5,491,261 discloses several other glycols that can benefit from the  $R_f$  group of the present invention and is herein incorporated by reference.

**[0070]** Exemplary diols having  $R_f$  groups of the present invention can be converted to phosphoric acid functionality or phosphate esters (not shown). U.S. Patent 5,091,550, 5,132,445, 4,898,981, and 5,491,261 all disclose methods of preparing diols and converting glycols to phosphate esters and are herein incorporated by reference. In an exemplary implementation, the glycols can be converted to phosphoric acid or phosphate esters by reacting the glycols in the presence of phosphoric acid. These compositions can be incorporated into compounds which can act as oil and grease proofing for paper as well as soil release agents for textile fibers.

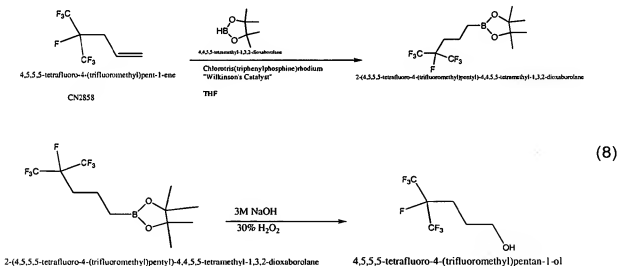
**[0071]** Referring to Fig. 5, multiple reactions sequences 70 are shown for the preparation of an acrylic monomer 80 having the  $R_f$  group of the present invention. U.S. Patents 3,491,169, 3,282,905, 3,497,575, 3,544,663, 6,566,470, 4,147,851, 4,366,299 and 5,439,998 all relate to the use and preparation of acrylic emulsion polymers that can benefit from the  $R_f$  group



of the present invention and are herein incorporated by reference. Thiol  $R_f$  intermediates 72, iodine  $R_f$  intermediate 74, hydroxyl  $R_f$  intermediates 76, and/or acetate  $R_f$  intermediates 78 can be converted to acrylate monomer 80 according to the schemes and references described herein.

**[0072] Exemplary preparation of 4,5,5,5-Tetrafluoro-4-(trifluoromethyl)pentyl acrylate**

**[0073]** The acrylate 4,5,5,5-Tetrafluoro-4-(trifluoromethyl)pentyl acrylate is prepared from the  $R_f$  intermediate 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene in two steps shown below as reaction sequence (8) and (9) respectively.



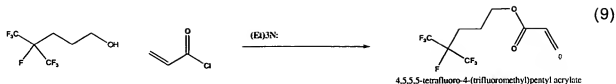
**[0074]** A 1M solution of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane in tetrahydrofuran (66.1g, 0.075 moles), chlorotris(triphenylphosphine)rhodium

(0.37g), and Tetrahydrofuran (158.8g) is placed in a 500mL three-neck round bottom flask (RBF). 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene (18.243, 0.087 moles) is added to reaction mixture at room temperature over a 15 minute period. Reaction is carried out for 72 hours and is monitored by gas chromatography until which time the 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene is substantially consumed (See Table 1 below for monitoring of reaction).

Table 1: Formation of Borate Ester Reaction Monitoring by Gas Chromatography; All Samples Analyzed on DB WAX Column.			
Sample Number	3.07 minute Area %	9.3 minute Area %	16.8 minute Area %
1	57	29	14
2	22	11	66
3	0	5.4	94.5

Note: 3.07 minute peak = 4,5,5,5-tetrafluoro-4-(trifluoromethyl)pent-1-ene, 9.3 minute peak = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 16.8 minute peak = 2-(4,5,5,5-tetrafluoro-4-(trifluoromethyl)pentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan

**[0075]** A 3M aqueous solution of Sodium Hydroxide (7.8g) is added to the reaction mixture via the addition funnel over a 15 minute period after which the reaction mixture is chilled to 0°C using an ice bath. Hydrogen peroxide (23.6g, 35% aqueous solution) is added dropwise over a 15 minute period to the reaction mixture. The reaction mixture is then washed in H<sub>2</sub>O three times. The organic mixture is transferred into a 100mL 3-neck RBF and distilled to produce an 85% pure (by gas chromatography) 4,5,5,5-Tetrafluoro-4-(trifluoromethyl)pentan-1-ol having a DB Wax elution time of 19.7 minutes.



**[0076]** The 4,5,5,5-Tetrafluoro-4-(trifluoromethyl)pentan-1-ol (2.59g, 0.011moles) and triethylamine (1.3g, 0.013 moles) are added to a 15mL three-neck RBF. The RBF contents are chilled to 0°C using ice water bath and acryloyl chloride (1.38g, 0.015 moles) is added dropwise using an addition funnel to the RBF over a 15 minute period. After a 1 hour hold period, 10 mL H<sub>2</sub>O is added and two phases were observed. Water is decanted off the reaction mixture and organic phase is dried over MgSO<sub>4</sub>. Organic phase is analyzed by GC wherein a peak was observed at 16.1 minutes on DB Wax Column. GC/MS confirm that the new peak has a mass of 283.

**[0077]** For example and by way of example only, the R<sub>f</sub> group of the present invention can be incorporated into a monomer as described in U.S. Patent 6,566,470 represented as R<sub>f</sub>-W-X-C(=O)-C(R<sup>1</sup>)=CH<sub>2</sub> with the R<sub>f</sub> group as described above, W can be an alkylene with 1 to 15 carbons, hydroxyalkylene with 3 to 15 carbons, -(C<sub>n</sub>H<sub>2n</sub>)(OC<sub>m</sub>H<sub>2m</sub>)<sub>q</sub>-, -SO<sub>2</sub>NR<sup>2</sup>-(C<sub>n</sub>H<sub>2n</sub>)- or -CONR<sup>2</sup>-(C<sub>n</sub>H<sub>2n</sub>)-, with n is 1 to 12, m is 2 to 4, q is 1 to 10 and R<sup>1</sup> is an alkyl group with 1 to 4 carbon atoms, X can be O, S and/or N(R<sup>2</sup>), where R<sup>2</sup> is as R<sup>1</sup> as defined above. This monomer can be incorporated with other monomers and then incorporated into the

construction of paper materials or used to treat paper materials. These polymeric solutions can be diluted to a percentage aqueous or non-aqueous solution and then applied to substrates to be treated such as paper plates.

**[0078]** Monomers having the  $R_f$  group of the present invention can also be incorporated into copolymers with comonomers such as the dialkyl amino alkyl acrylate or methacrylate or acrylamide or methacrylamide monomer and its amine salt quaternary ammonium or amine oxide form as described in U.S. Patent 4,147,851, herein incorporated by reference. The general formula for these  $R_f$  acrylates can be  $R_fqO_2CC(R)=CH_2$  wherein R is H or  $CH_3$ , q is an alkylene of 1 to 15 carbon atoms, hydroxyalkylene of 3 to 15 carbon atoms, or  $C_nH_{2n}(OC_qH_{2q})_m$ -,  $-SO_2NR^1(C_nH_{2n})$ -, or  $-CONR^1(C_nH_{2n})$ -, n is 1 to 15, q is 2 to 4 and m is 1 to 15. Comonomers forming a copolymer with acrylates having the  $R_f$  group described above include those having amine functionality. These copolymers can be diluted in a solution and applied or incorporated directly into or on substrates to be treated such as paper.

**[0079]**  $R_f$  groups of the present invention can also be incorporated into acrylate polymers or other acrylate monomers consistent with those described in U.S. Patent 4,366,299, herein incorporated by reference. These compositions can be incorporated into paper products or applied thereon.

**[0080]** Acrylics having  $R_f$  groups of the present invention can be applied to finished carpet or incorporated into the finished carpet fiber before it is woven into carpet. Acrylics having  $R_f$  groups of the present invention can be applied to carpet by a normal textile finishing process known as padding, in which the carpet is passed through a bath containing latex, water and other minor additives such as non-rewetting surfaces. The carpet can then be passed through nip rollers to control the rate of the add-on before being dried in a tenter frame. The acrylics of the present invention may also be incorporated into the fiber by reacting the fiber with isocyanates having the  $R_f$  group of the present invention.

**[0081]** The  $R_f$  groups of the present invention can also be incorporated into materials used to treat calcitic and/or siliceous particulate materials. The  $R_f$  groups of the present invention can be incorporated as a monomer into a copolymer where the copolymer can either be part of a formulation to treat these materials or used by itself to treat these materials as described in U.S. Patent 6,383,569 herein incorporated by reference. The monomer can have the general formula  $R_f-Q-A-C(O)-C(R)=CH_2$  wherein  $R_f$  is described above, R is H or  $CH_3$ , A is O, S, or  $N(R')$ , wherein  $R'$  is H or an alkyl of from 1 to 4 carbon atoms, Q is alkylene of 1 to about 15 carbon atoms, hydroxyalkylene of 3 to about 15 carbon atoms,  $-(C_nH_{2n})(OC_qH_{2q})_m-$ ,  $-SO_2-NR'(C_nH_{2n})-$ , or  $-CONR'(C_nH_{2n})-$ , wherein  $R'$  is H or an alkyl of 1 to 4 carbon atoms, n is 1 to 15, q is 2 to 4, and m is 1 to 15.

**[0082]** Once these compositions and mixtures contain the  $R_f$  group of the present invention, they can be used to treat hard surfaces including construction materials such as brick, stone, wood, concrete, ceramics, tile, glass, stucco, gypsum, drywall, particle board and chipboard. As stated above, they can be used alone or as in combination with penetration assistance such as non-ionic surfactants. These compositions can be applied to the surface of calcitic and/or siliceous architectural construction material by any known method, for example, by soaking, impregnation, emersion, brushing, rolling, or spraying. Compositions including the  $R_f$  groups of the present invention can be applied to the surface to be protected by spraying. Suitable spraying equipment is commercially available. Spraying with a compressed air sprayer is the preferred method of application to the particular material. U.S. Patents 6,197,382 and 5,674,961 also describes methods for applying and using polymer solutions and are herein incorporated by reference.

**[0083]** In an exemplary process of producing solutions having components with  $R_f$  groups according to the present invention, an  $R_f$  group may be attached to a methyl-epoxide group and the epoxide condensed with a monocarboxylic alkenoic acid to prepare an unsaturated ester (not shown). Exemplary methods for producing these kinds of unsaturated esters are described in U.S. Patent 5,798,415 herein incorporated by reference. Additional esters may be prepared according to U.S. Patent 4,478,975 herein incorporated by reference. Components of these solutions can also

include dimethyl amino ethyl methacrylate and these components can be applied in organic and inorganic solvents, as described in U.S. Patent 6,120,892 herein incorporated by reference.  $R_f$  group polymers and copolymers can also be combined with monomers to produce copolymers or in solutions with amido and sulfur monomers represented by U.S. Patent 5,629,372 herein incorporated by reference.

**[0084]** Amine  $R_f$  intermediates can also be reacted with tetrachlorophthalic anhydride using U.S. Patent 4,043,923 as an exemplary reaction scheme, U.S. Patent 4,043,923 is herein incorporated by reference (not shown). The reaction product can be mixed with a carpet cleaning solution to provide soil repellency.

**[0085]** The  $R_f$  group of the present invention may also be incorporated into urethanes. Referring to Fig. 6 a reaction sequence 90 is shown for the preparation of urethanes including the  $R_f$  group of the present invention. A hydroxyl  $R_f$  intermediate 92 can be combined with hexamethylene diisocyanate polymers (DESMODUR N-100) 94 following the general reaction sequence described in U.S. Patent 5,827,919 herein incorporated by reference to produce urethane 96. Another method for preparing the urethanes of the present invention includes reacting a mercaptan  $R_f$  intermediate with epichlorohydrin to produce a "twin tailed" which can be reacted with diisocyanate and/or a urethane prepolymer as described in U.S. patent 4,113,748 herein incorporated by reference (not shown). The

urethanes having the  $R_f$  group can then be incorporated as an additive to compositions such as latex paint. U.S. Patent 5,827,919 described methods for utilizing these urethanes and is herein incorporated by reference. Urethanes and polyurethanes can be used to treat substrates such as carpet, drapery, upholstery, automotive and awning fabrics, and rainwear.

**[0086]** The  $R_f$  group can also be complexed as an acid with amine and quaternary ammonium polymers as described in U.S. Patent 6,486,245 herein incorporated by reference (not shown).

**[0087]** In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect.



**[0088]** Aspects of the Invention.

**[0089]** 1.  $R_f$  groups having at least two terminal  $-CF_3$  groups with at least half of the fluorine content of the  $R_f$  group being provided by the  $-CF_3$  groups.

**[0090]** 2. The  $R_f$  groups of 1 incorporated into polymers, urethanes, acrylate polymers, acrylate monomers, glycols, phosphate esters, metal complexes, and/or fluorosurfactant compositions.

**[0091]** 3. The compositions of 2 used as disbursing agents; treatments for substrate materials such as textile fabric, textile yarns, leather, paper, plastic, sheeting, wood, ceramic clays, as well as articles of apparel, wallpaper, paper bags, cardboard boxes, porous earthenware, construction materials such as brick, stone, wood, concrete, ceramics, tile, glass, stucco, gypsum, drywall, particle board and chipboard, and substrates such as carpet, drapery, upholstery, automotive and awning fabrics, and rainwear.

**[0092] ABSTRACT OF THE DISCLOSURE**

**[0093]** The present invention provides  $R_f$  groups can have at least two terminal  $-CF_3$  groups with at least half of the fluorine content of the  $R_f$  group provided by the  $-CF_3$  groups. An exemplary general structure for the  $R_f$  group includes  $(CF_3)_n(CF)_{(3-n)}(CF_2)_m$ , with  $n$  between 1 and 3 and  $m$  between 0 and 6. These  $R_f$  groups can be incorporated compositions such as polymers, urethanes, acrylate polymers, acrylate monomers, glycols, phosphate esters, metal complexes, and fluorosurfactants. These compositions can be used as disbursing agents, to treat substrate materials such as textile fabric, textile yarns, leather, paper, plastic, sheeting, wood, ceramic clays, as well as articles of apparel, wallpaper, paper bags, cardboard boxes, porous earthenware, construction materials such as brick, stone, wood, concrete, ceramics, tile, glass, stucco, gypsum, drywall, particle board and chipboard, and substrates such as carpet, drapery, upholstery, automotive and awning fabrics, and rainwear.

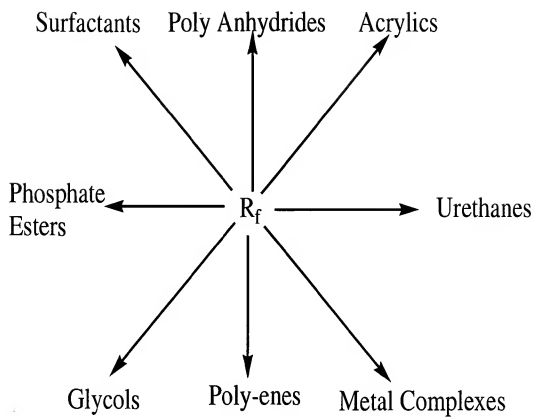


Figure 1

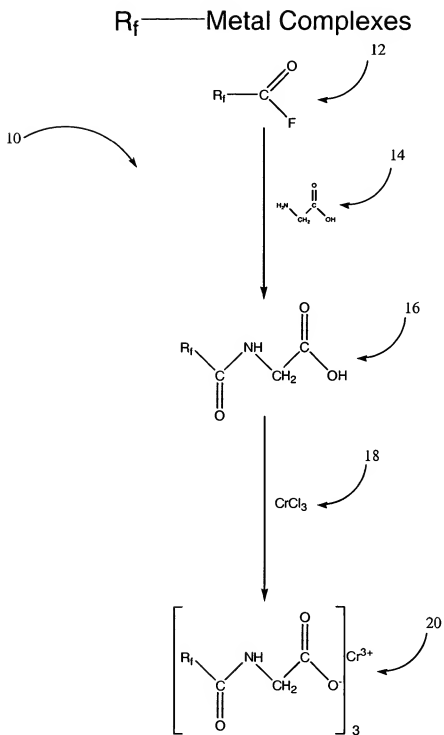


Figure 2

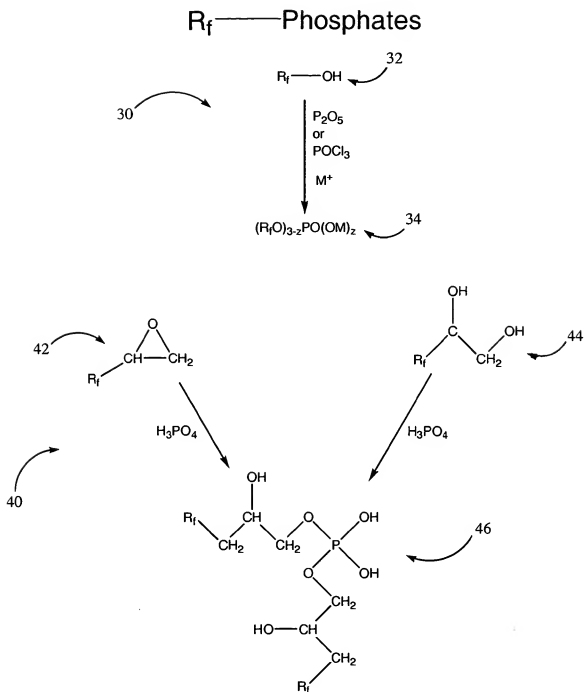


Figure 3

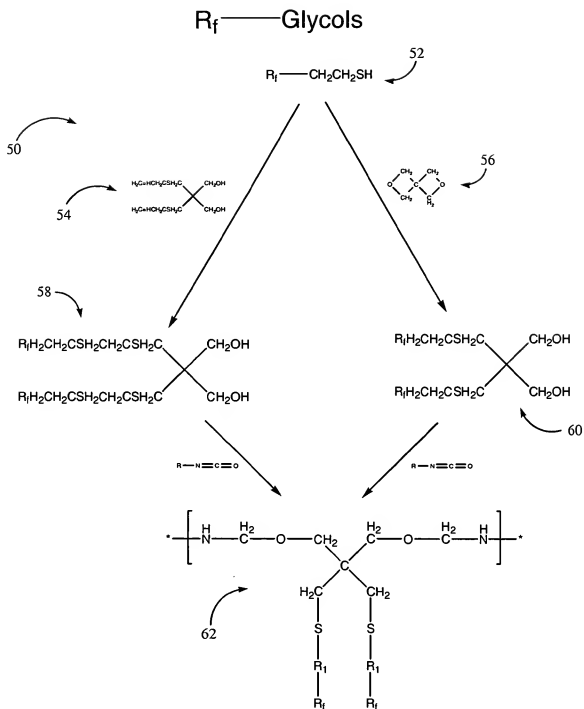


Figure 4

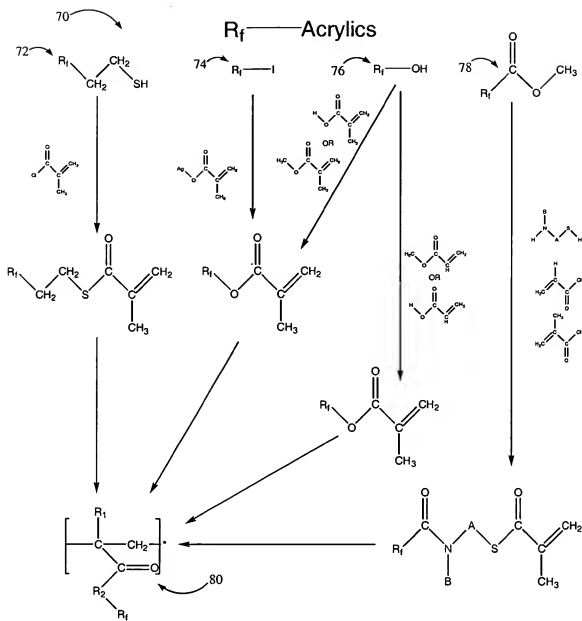


Figure 5

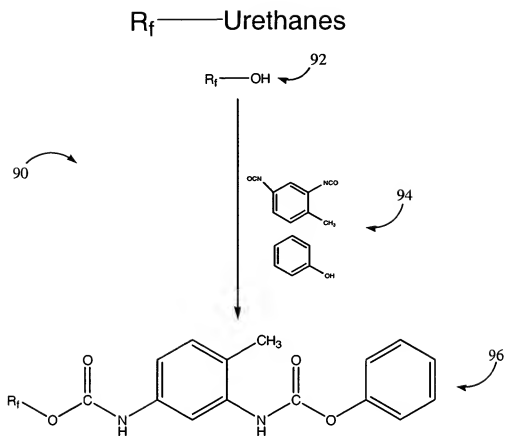


Figure 6